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Articles

Studies of the Coupling of Aryl Isothiocyanates to Bridging Alkyne Ligands in Dirhenium Carbonyl Complexes

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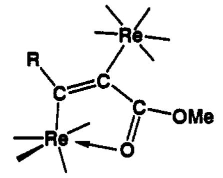
Reactions of the lightly stabilized dimetalated olefin complex $Re(CO)_4[\textit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_4(NCMe)$ (1) with aryl isothiocyanates have yielded a series of complexes having the general formula $Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)CN(Ar){=}S]Re(CO)_4$ (**2a**, Ar = *p*-tolyl; **2b**, Ar = Ph; **2c**, Ar = *p*-chlorophenyl). Compounds **2a–c** were formed by the loss of NCMe from 1 and the addition and insertion of one isothiocyanate molecule into one of the metal–carbon bonds to form a thioamido group that is chelated to one of the rhenium atoms. When heated to 98 °C, complexes **2a–c** were decarbonylated and converted into the dimeric complexes $[Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)CN(Ar){=}S]Re(CO)_3]_2$ (**3a**, Ar = *p*-tolyl; **3b**, Ar = Ph; **3c**, Ar = *p*-chlorophenyl), in which the sulfur atoms of the thioamido groups bridge the two metal atoms. Decarbonylation of **2a–c** at 80 °C in the presence of $[Re(CO)_4(\mu\text{-}I)]_2$ yielded the trirhenium complexes $Re(CO)_4[\mu\text{-}(E)\text{-}HC{=}C(CO_2Me)CN(Ar){=}S]Re_2(CO)_7(\mu\text{-}I)$ (**4a**, Ar = *p*-tolyl; **4b**, Ar = Ph; **4c**, Ar = *p*-chlorophenyl). These complexes contain a $Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)\text{-}CN(Ar){=}S]Re(CO)_3$ grouping similar to that found in the free molecules **2a–c** but also have a $Re(CO)_4I$ grouping joined to the complex through a bridging thioamido sulfur atom and a bridging iodo ligand. Complexes 1, **2a**, **3a**, and **4c** were characterized by single-crystal X-ray diffraction analyses. Crystal data: for 1, space group $P\bar{1}$, $a = 9.272(1)$ Å, $b = 13.122(2)$ Å, $c = 8.509(1)$ Å, $\alpha = 106.46(1)^\circ$, $\beta = 95.78(1)^\circ$, $\gamma = 69.85(1)^\circ$, $Z = 2$, 2097 reflections, $R = 0.038$; for **2a**, space group $P2_1/c$, $a = 10.317(1)$ Å, $b = 15.819(2)$ Å, $c = 15.448(3)$ Å, $\beta = 103.26(1)^\circ$, $Z = 4$, 2415 reflections, $R = 0.027$; for **3a**, space group $P\bar{1}$, $a = 10.361(2)$ Å, $b = 12.638(2)$ Å, $c = 9.318(2)$ Å, $\alpha = 91.36(2)^\circ$, $\beta = 102.72(2)^\circ$, $\gamma = 78.14(1)^\circ$, $Z = 2$, 1439 reflections, $R = 0.031$; for **4c**, space group *Pbca*, $a = 19.910(4)$ Å, $b = 24.294(4)$ Å, $c = 12.901(2)$ Å, $Z = 8$, 2716 reflections, $R = 0.029$.

Introduction

Metal complexes have been shown to be valuable agents for the activation and modification of organic isocyanates.[1] Organic isothiocyanates are useful reagents in organic synthesis,[2] but the organometallic chemistry of these molecules has not yet been well studied.[3]

We have recently shown that alkyne ligands containing carboxylate groups, $RC{\equiv}CCO_2R'$ (R = H, Me, CO_2Et), adopt the *trans*-dimetalated olefin structure in the dirhenium complexes $Re(CO)_4[\textit{trans}\text{-}\mu\text{-}RC{=}C(CO_2Me)]Re(CO)_5$ (**A**) after the insertion of the alkyne into the metal–metal bond of the complex $Re_2(CO)_9(NCMe)$.[4] The complexes are stabilized in part by the coordination of the ketonic oxygen atom of the carboxylate group.



A

When treated with Me_3NO in the presence of acetonitrile, $Re(CO)_4[\textit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_5$ is transformed into the lightly stabilized complex $Re(CO)_4[\textit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_4(NCMe)$ (1). Complex 1 readily reacts with carboxylate-substituted alkynes to form oligomeric chains of the alkynes by head-to-tail coupling reactions.[5]

We have now found that 1 reacts with aryl isothiocyanates by addition and insertion of the isothiocyanate molecule into the carboxylate-substituted Re–C bonds to form the new complexes $Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)\text{-}CN(Ar){=}S]Re(CO)_4$ (**2a**, Ar = *p*-tolyl; **2b**, Ar = Ph; **2c**, Ar = *p*-chlorophenyl). Compounds **2a–c** are decarbonylated upon mild heating to form dimers, $[Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)CN(Ar){=}S]Re(CO)_3]_2$ (**3a–c**). They also react with $[Re(CO)_4(\mu\text{-}I)]_2$ to yield the new trirhenium complexes $Re(CO)_4[\mu\text{-}(E)\text{-}HC{=}C(CO_2Me)CN(Ar){=}S]\text{-}Re_2(CO)_7(\mu\text{-}I)$ (**4a–c**). The results of this study are

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[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1993.

[1] Braunstein, P.; Nobel, D. *Chem. Rev.* **1989,** *89,* 1927.

[2] Mukerjee, A. K.; Ashare, R. *Chem. Rev.* **1991,** *91,* 1.

[3] Werner, H. *Coord. Chem. Rev.* **1982,** *43,* 165.

[4] (a) Adams, R. D.; Chen, L.; Wu, W. *Organometallics* **1993,** *12,* 1257. (b) Adams, R. D.; Chen, L.; Wu, W. *Organometallics* **1992,** *11,* 3505.

[5] Adams, R. D.; Chen, L.; Wu, W. *Organometallics* **1993,** *12,* 1623.

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reported here. A preliminary report of a portion of this work has been published.[6]

Experimental Section

All reactions were carried out under an atmosphere of nitrogen. Hexane and heptane were freshly distilled over sodium before use. CH$_2$Cl$_2$ was stored over CaH$_2$. (*p*-tolyl)NCS, PhNCS, and (*p*-chlorophenyl)NCS were purchased from Aldrich Chemical Co. and were used without further purification. TLC separations were performed in air by using silica gel (60 Å, F$_{254}$) on plates (Whatman, 0.25 mm). IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^{1}H NMR spectra were taken at 300 MHz on a Bruker AM-300 spectrometer. Mass spectra were run on a VG Model 70SQ mass spectrometer using electron impact ionization. Elemental analyses were performed by Desert Analytics, Tucson, AZ. (OC)$_4$Re[*trans*-μ-HC=C(CO$_2$Me)]Re(CO)$_4$(MeCN) (**1**)[5] and [Re(CO)$_4$(μ-I)]$_2$[7] were prepared by previously reported procedures.

Preparation of (OC)$_4$Re[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_4$-*p*-Me)=S]Re(CO)$_4$ (2a). A 10.0-mg amount (0.014 mmol) of **1** and a 10.4-mg amount (0.070 mmol) of (*p*-tolyl)NCS were dissolved in 20 mL of CH$_2$Cl$_2$. The solution was heated to reflux for 3 h. After the solution was cooled, the solvent was evaporated under vacuum. The residue was separated using a hexane/CH$_2$Cl$_2$ (4/1) solvent mixture to give 6.7 mg of pale yellow (OC)$_4$Re[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_4$-*p*-Me)=S]Re(CO)$_4$ (**2a**) in 58% yield. IR (ν_{CO} in hexane, cm^{-1}) for **2a**: 2099 (w), 2003 (s), 1994 (m), 1989 (m), 1952 (s), 1591 (w). ^{1}H NMR (δ in CDCl$_3$, ppm) for **2a**: 10.45 (s, 1H, C*H*), 7.04 (d, $^3J_{H-H}$ = 8.0 Hz, 2H, C$_6$*H*$_4$), 6.73 (d, $^3J_{H-H}$ = 8.3 Hz, 2H, C$_6$*H*$_4$), 3.48 (s, 3H, O*Me*), 2.29 (s, 3H, C$_6$H$_4$*Me*). Anal. Calcd (found) for **2a** (Re$_2$SO$_{10}$NC$_{20}$H$_{11}$): C, 28.92 (29.12); H, 1.33 (1.21); N, 1.69 (1.47). Compounds **2b,c** were prepared similarly.

(OC)$_4$Re[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_5$)=S]Re(CO)$_4$ (2b): pale yellow solid, 64%. IR (ν_{CO} in hexane, cm^{-1}): 2100 (w), 2004 (s), 1995 (s), 1991 (s), 1953 (s), 1589 (w, br). ^{1}H NMR (δ in CDCl$_3$, ppm): 10.48 (s, 1H, C*H*), 7.26 (m, 2H, C$_6$*H*$_5$), 7.11 (m, 1H, C$_6$*H*$_5$), 6.85 (m, 2H, C$_6$*H*$_5$), 3.47 (s, 3H, O*Me*). The mass spectrum showed a parent ion at *m*/*e* 817 for ^{187}Re and the ions corresponding to the loss of each of the eight carbonyl ligands.

(OC)$_4$Re[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_4$-3-Cl)=S]Re(CO)$_4$ (2c): pale yellow solid, 77% yield. IR (ν_{CO} in hexane, cm^{-1}): 2100 (w), 2005 (s), 1992 (s), 1954 (s), 1588 (w, br). ^{1}H NMR (δ in CDCl$_3$, ppm): 10.53 (s, 1H, C*H*), 7.23 (d, $^3J_{H-H}$ = 8.7 Hz, 2H, C$_6$*H*$_4$), 6.80 (d, $^3J_{H-H}$ = 8.7 Hz, 2H, C$_6$*H*$_4$), 3.54 (s, 3H, O*Me*). The mass spectrum showed a parent ion at *m*/*e* 851 for ^{187}Re and the ions corresponding to the loss of each of the eight carbonyl ligands.

Preparation of {(OC)$_4$Re[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_4$-*p*-Me)=S]Re(CO)$_3$}$_2$ (3a): A 10.0-mg amount (0.012 mmol) of **2a** dissolved in 25 mL of heptane was heated to reflux for 30 min. A pale yellow precipitate formed during this period. After the solution was cooled to room temperature, the solvent was evaporated. The residue was redissolved in the minimum amount of CH$_2$Cl$_2$ and cooled to −14 °C to give 8.1 mg (84% yield) of pale yellow crystals of {(OC)$_4$Re[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_4$-*p*-Me)=S]Re(CO)$_3$}$_2$ (**3a**). Attempts to purify **3a** by TLC resulted in its decomposition. IR (ν_{CO} in CH$_2$Cl$_2$, cm^{-1}): 2103 (w), 2020 (s), 2003 (m, br), 1940 (m, br), 1922 (m, br), 1593 (w, br). ^{1}H NMR (δ in CDCl$_3$, ppm): 11.17 (s, 2H, C*H*), 7.16 (d, $^3J_{H-H}$ = 8.4 Hz, 4H, C$_6$*H*$_4$), 6.97 (d, $^3J_{H-H}$ = 8.4 Hz, 4H, C$_6$*H*$_4$), 3.40 (s, 6H, O*Me*), 2.36 (s, 6H, C$_6$H$_4$*Me*). Anal. Calcd (found) for **3a** (Re$_4$S$_2$O$_{18}$N$_2$C$_{38}$H$_{22}$): C, 28.44 (27.70); H, 1.37 (1.04); N, 1.75 (1.67). Compounds **3b,c** were prepared similarly.

{(OC)$_4$Re[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_5$)=S]Re(CO)$_3$}$_2$ (3b): pale yellow solid, 87% yield. IR (ν_{CO} in CH$_2$Cl$_2$, cm^{-1}): 2103 (w), 2021 (s), 2004 (m, br), 1940 (m, br), 1926 (m, br), 1590 (w, br). ^{1}H NMR (δ in CDCl$_3$, ppm): 11.23 (s, 2H, C*H*), 7.38 (d, m, 4H, C$_6$*H*$_5$), 7.26 (m, 2H, C$_6$*H*$_5$), 7.08 (m, 4H, C$_6$*H*$_5$), 3.38 (s, 6H, O*Me*). The mass spectrum of **3b** showed a parent ion at *m*/*e* 1578 for ^{187}Re and the ions corresponding to the loss of each of the nine carbonyl ligands.

{(OC)$_4$Re[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_4$-3-Cl)=S]Re(CO)$_3$}$_2$ (3c): pale yellow crystals, 80% yield. IR (ν_{CO} in CH$_2$Cl$_2$, cm^{-1}): 2104 (w), 2022 (s), 2003 (m, br), 1942 (m, br), 1926 (m, br), 1594 (w, br). ^{1}H NMR (δ in CDCl$_3$, ppm): 11.30 (s, 2H, C*H*), 7.36 (d, $^3J_{H-H}$ = 8.8 Hz, 4H, C$_6$*H*$_4$), 7.02 (d, $^3J_{H-H}$ = 8.8 Hz, 4H, C$_6$*H*$_4$), 3.47 (s, 6H, O*Me*).

Reaction of {(OC)$_4$Re[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_4$-*p*-Me)=S]Re(CO)$_3$}$_2$ (3a) with CO. After a 10.0-mg (0.0062-mmol) amount of **3a** was dissolved completely in 30 mL of CH$_2$Cl$_2$, the solution was bubbled with 1 atm of CO at 25 °C for 12 h. The solvent was removed by evaporation under vacuum. The residue was separated by TLC with a hexane/CH$_2$Cl$_2$ (1/1) solvent mixture to give 8.8 mg of **2a**; 85% yield.

Preparation of Re$_3$(CO)$_{11}$(μ-I)[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_4$-*p*-Me)=S] (4a). A 10.0-mg amount (0.012 mmol) of **2a** and a 20.0-mg amount (0.024 mmol) of [Re(CO)$_4$(μ-I)]$_2$ were dissolved in 30 mL of heptane. The solution was heated at 80 °C for 5 h. After it was cooled to room temperature, the solution was evaporated to dryness. The residue was separated by using a hexane/CH$_2$Cl$_2$ (1/1) solvent mixture to give the following compounds in order of elution: 2.1 mg of starting material, **2a**; 9.6 mg of pale yellow Re$_3$(CO)$_{11}$(μ-I)[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_4$-*p*-Me)=S] (**4a**), 67% yield; 7.4 mg of [Re(CO)$_4$(μ-I)]$_2$. IR (ν_{CO} in hexane, cm^{-1}) for **4a**: 2111 (w), 2102 (w), 2035 (s), 2020 (m), 2006 (m), 2000 (m), 1993 (s), 1967 (s), 1957 (m), 1938 (m), 1929 (m), 1595 (w, br). ^{1}H NMR (δ in C$_6$D$_6$, ppm): 10.42 (s, 1H, C*H*), 6.87 (d, $^3J_{H-H}$ = 8.5 Hz, 2H, C$_6$*H*$_4$), 6.78 (d, $^3J_{H-H}$ = 8.5 Hz, 2H, C$_6$*H*$_4$), 2.71 (s, 3H, O*Me*), 1.94 (s, 3H, C$_6$H$_4$*Me*). The mass spectrum of **4a** showed a parent ion at *m*/*e* = 12279 for ^{187}Re and the ions corresponding to the loss of each of the 11 carbonyl ligands.

Preparation of Re$_3$(CO)$_{11}$(μ-I)[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_5$)=S] (4b). A 10.0-mg amount (0.012 mmol) of **2b** and a 20.0-mg amount (0.024 mmol) of [IRe(CO)$_4$]$_2$ were dissolved in 30 mL of heptane. The solution was heated at 80 °C for 5 h. Separation as described above gave the following result: 1.8 mg of starting material, **2b**; 9.8 mg of pale yellow Re$_3$(CO)$_{11}$(μ-I)[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_5$)=S] (**4b**) 67% yield; 7.8 mg of [IRe(CO)$_4$]$_2$. IR (ν_{CO} in hexane, cm^{-1}) for **4b**: 2111 (w), 2103 (w), 2035 (s), 2020 (m), 2008 (m), 2003 (m), 1994 (s), 1967 (s), 1956 (m), 1947 (m), 1937 (m), 1929 (m), 1593 (w, br). ^{1}H NMR (δ in CDCl$_3$, ppm): 11.06 (s, 1H, C*H*), 7.36 (m, 2H, C$_6$*H*$_5$), 7.25 (m, 1H, C$_6$H$_5$), 7.18 (m, 2H, C$_6$*H*$_5$), 3.45 (s, 3H, O*Me*). The mass spectrum of **4b** showed a parent ion at *m*/*e* 1215 for ^{187}Re and the ions corresponding to the loss of each of the 11 carbonyl ligands.

Preparation of Re$_3$(CO)$_{11}$(μ-I)[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_4$-*p*-Cl)=S] (4c). A 10.0-mg amount (0.012 mmol) of **2c** and a 20.0-mg amount (0.024 mmol) of [IRe(CO)$_4$]$_2$ were dissolved in 30 mL of heptane. The solution was heated at 80 °C for 5 h. Separation, as described above, gave the following result: 1.9 mg of starting material, **2c**; 10.1 mg of pale yellow Re$_3$(CO)$_{11}$(μ-I)[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_4$-3-Cl)=S] (**4c**) 69% yield; and 7.1 mg of [IRe(CO)$_4$]$_2$. IR (ν_{CO} in hexane, cm^{-1}) for **4c**: 2110 (w), 2102 (w), 2036 (s), 2021 (m), 2008 (m), 2002 (m), 1993 (s), 1968 (s), 1959 (m), 1940 (m), 1931 (m), 1596 (w, br). ^{1}H NMR (δ in CDCl$_3$, ppm): 11.13 (s, 1H, C*H*), 7.34 (d, $^3J_{H-H}$ = 8.6 Hz, 2H, C$_6$*H*$_4$), 7.12 (d, $^3J_{H-H}$ = 8.7 Hz, 2H, C$_6$*H*$_4$), 3.55 (s, 3H, O*Me*). Anal. Calcd (found) for **4c** (Re$_3$IClSO$_{13}$NC$_{22}$H$_8$): C, 21.17 (21.73); H, 0.64 (0.57); N, 1.12 (1.67).

Crystallographic Analyses. Crystals of **1** suitable for X-ray diffraction analysis were grown from solution in methylene chloride solvent by slow evaporation of the solvent at −3 °C. Crystals of **2a** were grown from solution in a hexane/CH$_2$Cl$_2$ (1/1) solvent mixture at −3 °C. Crystals of **3a** were grown from a concentrated solution in CH$_2$Cl$_2$ by very slow evaporation at −3 °C. Crystals of **4c** were grown from solution in hexane/CH$_2$Cl$_2$ (3/1) at −3 °C. All crystals used in diffraction analyses were

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[6] Adams, R. D.; Chen, L.; Wu, W. *Organometallics* **1993**, *12*, 2404.

[7] Abel, E. W.; Hargreaves, G. B.; Wilkinson, G. *J. Am. Chem. Soc.* **1958**, *80*, 3149.

Table I. Crystallographic Data for Compounds 1, 2a, 3a, and 4c

	1	2a	3a	4c
empirical formula	$Re_2O_{10}NC_{14}H_7$	$Re_2SO_{10}NC_{20}H_{11}$	$Re_2SNO_9C_{19}H_{11}$	$Re_3IClSO_{13}NC_{22}H_8$
fw	721.62	829.78	801.77	1247.34
cryst syst	triclinic	monoclinic	triclinic	orthorhombic
lattice params				
a (Å)	9.272(1)	10.317(1)	10.361(2)	19.910(4)
b (Å)	13.122(2)	15.819(2)	12.638(2)	24.294(4)
c (Å)	8.509(1)	15.448(3)	9.318(2)	12.901(2)
α (deg)	106.46(1)		91.36(2)	
β (deg)	95.78(1)	103.26(1)	102.72(2)	
γ (deg)	69.85(1)		78.14(1)	
V (Å^3)	932.0(5)	2454(1)	1164.5(4)	6240(3)
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)
Z	2	4	2	8
D_{calc} (g/cm^3)	2.57	2.25	2.29	2.66
F_{000}	656	1536	740	4496
μ(Mo Kα) (cm^{-1})	132.04	101.24	106.60	129.60
temp (°C)	20	20	20	20
$2\theta_{max}$ (deg)	44.0	43.0	40.0	44.0
no. of observns ($I > 3\sigma(I)$)	2097	2415	1439	2716
no. of variables	247	327	289	379
residuals: R, R_w	0.038, 0.055	0.027, 0.029	0.031, 0.028	0.029, 0.027

mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromated Mo Kα radiation. Unit cells were determined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure-solving program library (version 5.0) obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[8a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[8b] Full matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

Compounds 1 and 3a crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of both structures. Both structures were solved by a combination of direct methods and difference Fourier syntheses. The coordinates of the metal atoms were obtained by direct methods (MITHRIL). All non-hydrogen atoms were subsequently obtained from difference Fourier syntheses, and all were refined with anisotropic thermal parameters. In the analysis of 1 the hydrogen atom H(3) was located and refined on its positional parameters. The positions of all other hydrogen atoms in 1 and all in 3a were calculated by assuming idealized geometries and using observed positions whenever possible for both analyses. The scattering contributions of the calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound 2a crystallized in the monoclinic crystal system. The space group $P2_1/c$ was established on the basis of the systematic absences observed during the collection of the intensity data. The structure was solved by a combination of direct methods and difference Fourier syntheses. The coordinates of the metal atoms were obtained by direct methods (MITHRIL). All non-hydrogen atoms were subsequently obtained from difference Fourier syntheses and were refined with anisotropic thermal parameters. Hydrogen atoms H(3), H(42), H(43), H(45), and H(46) were located and refined with isotropic thermal parameters. The positions of the hydrogen atoms on the methyl groups were calculated by assuming idealized geometries and using observed positions whenever possible. The scattering contributions of the calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

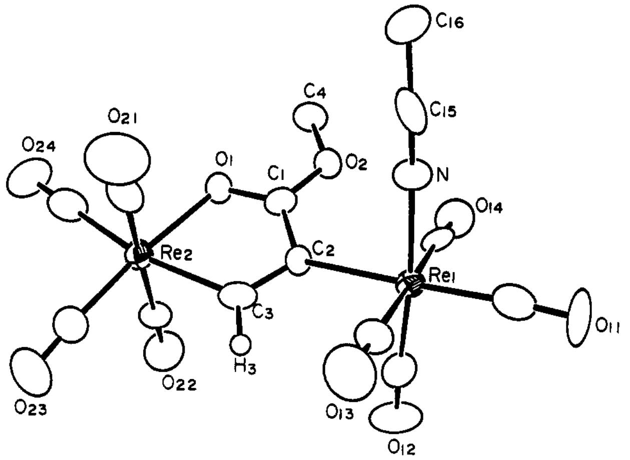

Figure 1. ORTEP diagram of Re(CO)$_4$[μ-HC=C(CO$_2$Me)]Re(CO)$_5$(NCMe) (1) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re(1)–N = 2.13(1), Re(1)–C(2) = 2.20(1), Re(2)–C(3) = 2.17(1), Re(2)–O(1) = 2.160(7), C(1)–C(2) = 1.47(2), C(2)–C(3) = 1.35(2), C(1)–O(1) = 1.30(1); Re(1)–C(2)–C(1) = 121.8(8), Re(2)–C(3)–C(2) = 119(1).

Compound 4c crystallized in the orthorhombic crystal system. The space group *Pbca* was established on the basis of the systematic absences observed during the collection of the intensity data. The structure was solved by a combination of direct methods and difference Fourier syntheses. The coordinates of the metal atoms were obtained by direct methods (MITHRIL). All non-hydrogen atoms were subsequently obtained from difference Fourier syntheses and were refined with anisotropic thermal parameters. The positions of all hydrogen atoms were calculated by assuming idealized geometries and using observed positions whenever possible. The scattering contributions of the calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Results

In order to develop a clearer understanding of the course of the reactions of 1 with donors, a crystal structure analysis of this compound was performed. An ORTEP diagram of the molecular structure of 1 is shown in Figure 1. Final fractional atomic coordinates are listed in Table II. The molecule is structurally very similar to that of its parent Re(CO)$_4$[*trans*-μ-HC=C(CO$_2$Me)]Re(CO)$_5$ (**A**).[4] The com-

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[8] (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99–101. (b) *Ibid.*, Table 2.3.1, pp 149–150.

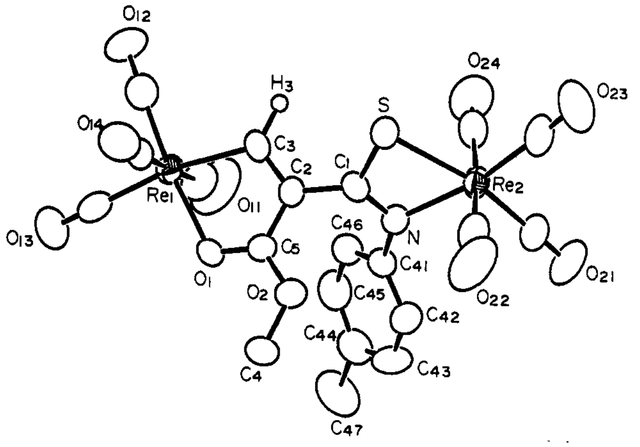


Figure 2. ORTEP diagram of Re(CO)$_4$[(*E*)-HC=C(CO$_2$Me)-CN(C$_6$H$_4$-*p*-Me)=S]Re(CO)$_4$ (**2a**) showing 35% probably thermal ellipsoids. Selected interatomic distances (Å): Re(1)–C(3) = 2.149(9), Re(1)–O(1) = 2.198(7), Re(2)–N = 2.178(7), Re(2)–S = 2.524(3), C(1)–C(2) = 1.49(1), C(2)–C(3) = 1.35(1), C(1)–N = 1.31(1), C(1)–S = 1.717(9), C(2)–C(5) = 1.44(1).

Table II. Positional Parameters and *B*(eq) Values for 1

atom	*x*	*y*	*z*	*B*(eq), Å^2
Re(1)	0.23985(04)	0.41246(03)	0.20636(05)	2.03(3)
Re(2)	0.21300(05)	0.07566(03)	0.40087(05)	2.34(3)
O(1)	0.3443(08)	0.1820(06)	0.5300(09)	2.4(4)
O(2)	0.4164(08)	0.3286(06)	0.5337(09)	2.6(4)
O(11)	0.2393(14)	0.5934(08)	0.0387(13)	5.8(7)
O(12)	−0.1004(11)	0.5299(09)	0.2924(14)	5.8(6)
O(13)	0.1611(13)	0.2559(09)	−0.1199(13)	5.5(6)
O(14)	0.3061(11)	0.5694(07)	0.5360(12)	4.4(5)
O(21)	0.4750(13)	0.0717(10)	0.1471(15)	6.8(7)
O(22)	−0.0823(12)	0.2347(08)	0.5998(12)	4.7(5)
O(23)	0.0119(11)	−0.0524(07)	0.1877(12)	4.5(5)
O(24)	0.3148(12)	−0.0799(09)	0.6340(16)	5.7(6)
N	0.4790(12)	0.3246(07)	0.1695(12)	2.6(5)
C(1)	0.3374(13)	0.2628(09)	0.4666(14)	2.4(5)
C(2)	0.2449(12)	0.2800(09)	0.3196(14)	2.1(5)
C(3)	0.1742(14)	0.2017(10)	0.2681(16)	2.8(6)
C(4)	0.4945(13)	0.3179(10)	0.6873(16)	3.3(6)
C(11)	0.2471(15)	0.5211(12)	0.0951(17)	3.7(7)
C(12)	0.0263(16)	0.4821(09)	0.2563(15)	3.2(7)
C(13)	0.1920(14)	0.3129(10)	−0.0008(16)	3.1(6)
C(14)	0.2841(13)	0.5083(09)	0.4164(17)	3.1(6)
C(15)	0.6072(17)	0.2754(11)	0.1534(14)	3.3(8)
C(16)	0.7722(14)	0.2124(11)	0.139(02)	4.7(7)
C(21)	0.3844(15)	−0.0198(10)	0.2433(18)	3.6(7)
C(22)	0.0302(13)	0.1766(09)	0.5349(15)	2.7(6)
C(23)	0.0898(13)	−0.0082(09)	0.2706(15)	2.8(6)
C(24)	0.2766(15)	−0.0234(12)	0.5505(17)	3.6(7)

plex can be described as a dimetalated olefin. The C(2)–C(3) distance of 1.35(2) Å is similar to that in **A**, 1.37(2) Å [1.41(2) Å], and is indicative of a C=C double bond. The rhenium atoms exhibit a *trans* or *E* stereochemistry with respect to the "olefinic" two carbon atoms. The ketonic oxygen atom O(1) of the ester grouping is coordinated to the metal atom Re(2) and forms a five-membered metallacyclic ring (Re(2)–O(1) = 2.160(7) Å). Most importantly, the linear acetonitrile ligand is coordinated to the rhenium atom Re(1) in a position *cis* to the carboxylate-substituted carbon atom of the dimetalated olefin grouping.

When **1** was treated with the series of aryl isothiocyanates RC$_6$H$_4$N=C=S (R = *p*-Me, H, *p*-Cl), (OC)$_4$Re[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_4$-*p*-R)=S]Re(CO)$_4$ (**2a–c**; R = *p*-Me, H, and *p*-Cl) were obtained in the yields 58, 64, and 77%, respectively. The ^{1}H NMR spectra of these compounds show the presence of the aryl groupings but are otherwise structurally uninformative. Thus, a single-crystal X-ray diffraction analysis of **2a** was performed to establish its molecular structure. An ORTEP diagram of the molecular structure of **2a** is shown in Figure 2. Final fractional atomic coordinates are listed in Table III. Compound **2a** contains two Re(CO)$_4$ groups that are linked by a bridging (*E*)-*N*-*p*-tolylthioamido, methyl carboxylate substituted vinyl group. The thioamido grouping is chelated to Re(2) (Re(2)–N = 2.178(7) Å and Re(2)–S =

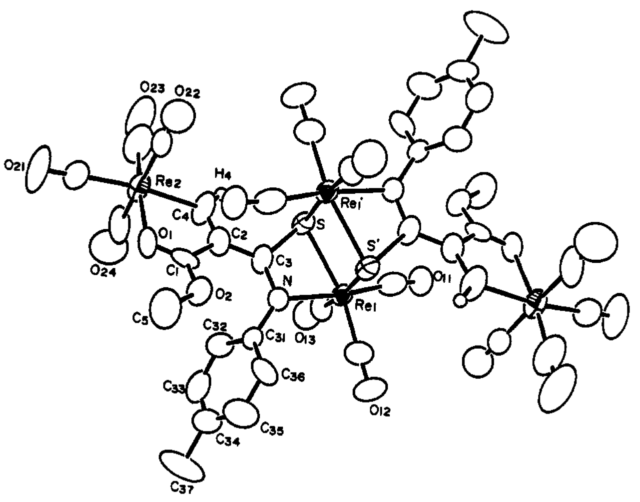


Figure 3. ORTEP diagram of {(OC)$_4$Re[(*E*)-HC=C(CO$_2$Me)C(NC$_6$H$_4$-*p*-Me)=S]Re(CO)$_3$}$_2$ (**3a**) showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg): Re(1)–S = 2.552(4), Re(1)′–S = 2.550(5), Re(1)–N = 2.15(1), Re(2)–O(1) = 2.18(1), Re(2)–C(4) = 2.12(2), C(1)–C(2) = 1.48(2), C(2)–C(3) = 1.46(2), C(3)–N = 1.31(2), C(3)–S = 1.79(2), C(2)–C(4) = 1.34(2), Re(1)···Re(1)′ = 3.960(2); Re(1)–S–Re(1)′ = 101.8(2), Re(1)–S–C(3) = 79.5(6), Re(1)′–S–C(3) = 96.6, S–C(3)–N = 108(1).

Table III. Positional Parameters and *B*(eq) Values for 2a

atom	*x*	*y*	*z*	*B*(eq), Å^2
Re(1)	−0.33385(04)	0.46227(03)	0.28416(03)	3.35(2)
Re(2)	0.25105(04)	0.23955(03)	0.51233(03)	3.39(2)
S	0.1121(03)	0.36770(16)	0.52754(17)	3.8(1)
O(1)	−0.3487(06)	0.3325(04)	0.3318(05)	4.2(3)
O(2)	−0.2398(06)	0.2299(04)	0.4162(05)	4.3(3)
O(11)	−0.2354(12)	0.3993(07)	0.1191(06)	9.4(6)
O(12)	−0.2809(08)	0.6456(05)	0.2344(05)	5.6(4)
O(13)	−0.6265(08)	0.4665(05)	0.1739(06)	7.5(5)
O(14)	−0.4265(08)	0.5394(05)	0.4465(05)	5.7(4)
O(21)	0.3632(09)	0.0700(05)	0.4655(05)	6.7(4)
O(22)	0.1280(11)	0.1535(06)	0.6564(07)	9.3(6)
O(23)	0.5122(09)	0.2717(06)	0.6506(06)	9.2(5)
O(24)	0.3610(10)	0.3373(06)	0.3669(06)	7.5(5)
N	0.0573(08)	0.2456(05)	0.4197(05)	3.5(4)
C(1)	0.0073(09)	0.3168(06)	0.4408(06)	3.1(4)
O(2)	−0.1233(09)	0.3534(06)	0.3947(06)	2.9(4)
C(3)	−0.1388(09)	0.4330(06)	0.3628(06)	3.3(4)
C(4)	−0.3582(11)	0.1786(07)	0.3973(09)	5.9(6)
C(5)	−0.2442(10)	0.3043(06)	0.3773(06)	3.2(4)
C(11)	−0.2717(13)	0.4205(08)	0.1785(08)	5.5(6)
C(12)	−0.3010(11)	0.5775(08)	0.2527(07)	4.5(5)
C(13)	−0.5207(13)	0.4649(06)	0.2157(08)	5.1(5)
C(14)	−0.3912(10)	0.5082(07)	0.3888(08)	4.0(5)
C(21)	0.3223(11)	0.1327(07)	0.4810(07)	4.6(5)
C(22)	0.1728(12)	0.1862(08)	0.6029(08)	5.4(6)
C(23)	0.4148(12)	0.2584(07)	0.6004(08)	5.3(6)
C(24)	0.3215(11)	0.3017(08)	0.4190(08)	4.6(6)
C(41)	−0.0055(09)	0.1962(06)	0.3449(06)	3.4(4)
C(42)	−0.0183(11)	0.1104(07)	0.3543(08)	4.6(5)
C(43)	−0.0816(13)	0.0629(08)	0.2804(10)	6.0(7)
C(44)	−0.1319(11)	0.1000(08)	0.1993(08)	4.8(6)
C(45)	−0.1114(11)	0.1849(09)	0.1913(08)	4.9(6)
C(46)	−0.0507(10)	0.2324(07)	0.2634(07)	3.9(5)
C(47)	−0.2086(13)	0.0476(09)	0.1202(09)	8.0(8)

Table IV. Positional Parameters and *B*(eq) Values for 3a

atom	*x*	*y*	*z*	*B*(eq), Å^2
Re(1)	0.69144(07)	0.45868(06)	0.48497(08)	3.40(5)
Re(2)	0.33508(09)	0.08984(07)	0.72924(09)	4.74(6)
S	0.4753(04)	0.3841(04)	0.4387(05)	3.5(3)
O(1)	0.4446(13)	0.1840(10)	0.8945(12)	4.4(8)
O(2)	0.5543(11)	0.3197(10)	0.9273(12)	4.5(7)
O(11)	0.7190(12)	0.5566(11)	0.1982(14)	5.3(8)
O(12)	0.9408(13)	0.5432(12)	0.6387(15)	6(1)
O(13)	0.8634(15)	0.2541(12)	0.3939(16)	7(1)
O(21)	0.2382(17)	−0.0275(13)	0.9609(20)	10(1)
O(22)	0.0821(17)	0.2793(15)	0.681(02)	9(1)
O(23)	0.196(02)	−0.0235(16)	0.469(02)	11(2)
O(24)	0.5850(18)	−0.0991(16)	0.752(02)	9(1)
N	0.6660(15)	0.3664(11)	0.6639(15)	3.6(8)
C(1)	0.4985(18)	0.2459(17)	0.843(02)	4(1)
C(2)	0.4921(18)	0.2555(14)	0.6841(19)	4(1)
C(3)	0.5541(20)	0.3310(14)	0.6199(17)	4(1)
C(4)	0.4196(20)	0.1880(16)	0.609(02)	5(1)
C(5)	0.553(02)	0.3175(19)	1.0818(18)	7(2)
C(11)	0.6993(18)	0.5241(17)	0.307(02)	5(1)
C(12)	0.8483(19)	0.5084(16)	0.5785(19)	4(1)
C(13)	0.7994(20)	0.3371(18)	0.433(02)	5(1)
C(21)	0.2728(20)	0.0126(18)	0.871(02)	5(1)
C(22)	0.173(02)	0.208(02)	0.702(02)	6(1)
C(23)	0.246(03)	0.020(02)	0.574(03)	8(2)
C(24)	0.489(03)	−0.0270(19)	0.745(03)	6(2)
C(31)	0.7677(16)	0.3252(15)	0.7919(17)	3(1)
C(32)	0.8231(18)	0.2148(17)	0.808(02)	4(1)
C(33)	0.929(02)	0.1826(19)	0.934(03)	6(2)
C(34)	0.9785(19)	0.253(02)	1.036(02)	6(1)
C(35)	0.919(02)	0.363(02)	1.013(03)	7(2)
C(36)	0.8153(19)	0.3994(16)	0.890(02)	5(1)
C(37)	1.096(02)	0.211(02)	1.163(02)	10(2)

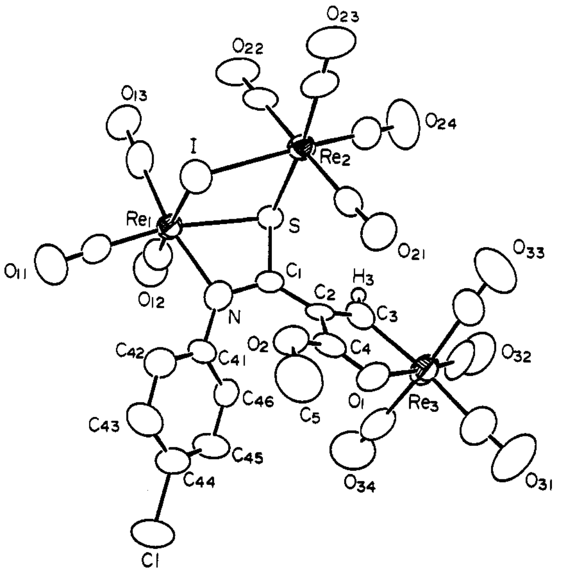


Figure 4. ORTEP diagram of $Re_3(CO)_{11}(\mu\text{-}I)[(E)\text{-}HC{=}C(CO_2Me)C(NC_6H_4\text{-}p\text{-}Cl){=}S]$ (**4c**) showing 50% probability thermal ellipsoids.

2.524(3) Å). The carboxylate group is coordinated by its ketonic oxygen atom to Re(1) as in 1 (Re(1)–O(1) = 2.198(7) Å). The C(2)–C(3) bond is a double bond (1.35(1) Å), and the C(1)–C(2) bond is a single bond (1.49(1) Å). The ligand is nonplanar. The planar Re(1), O(1), C(5), C(2), C(3) group is rotated 47.8° from the planar Re(2), N, C(1), S group. Compounds **2b,c** are believed to be structurally similar to **2a**.

When heated to reflux in heptane solvent, the compounds **2a–c** were decarbonylated and transformed into the new compounds $\{(OC)_4Re[(E)\text{-}HC{=}C(CO_2Me)C(NC_6H_4R){=}S]Re(CO)_3\}_2$ (**3a–c**; R = *p*-Me, H, *p*-Cl) in the yields 84%, 87%, and 80%, respectively. These compounds have low solubilities in common organic solvents; however, they can be recrystallized, and an X-ray structural characterization of **3a** was performed. An ORTEP diagram of the molecular structure of **3a** is shown in Figure 3. Final fractional atomic coordinates are listed in Table IV. This compound can be viewed as a dimer of a decarbonylated form of **2a**. The molecule is crystallographically centrosymmetrical, and the halves are linked through bridging sulfur atoms from the *p*-tolylthioamido groupings. These form a planar Re–S–Re–S rhombus (Re(1)–S = 2.552(4) Å and Re(1)′–S = 2.550(5) Å). The Re–Re distance of 3.960(2) Å is too long to permit any direct metal–metal bonding interactions. The nitrogen atom of the thioamido grouping is coordinated to one rhenium atom, one to each (Re(1)–N = 2.15(1) Å). The C–S bond distance in **3a** (C(3)–S = 1.79(2) Å) is significantly longer than that in **2a** (C(1)–S = 1.717(9) Å), where the sulfur is not a bridging atom. The C(2)–C(4) distance (1.34(2) Å) is indicative of a C═C double bond as in **2a**. The C(2)–C(3) distance (1.46(2) Å) is slightly shorter than the corresponding distance in **2a**. The carboxylate groups remain coordinated by their ketonic oxygen atoms (Re(2)–O(1) = 2.18(1) Å). The bridging ligand is nonplanar, and the dihedral angle between the planar Re(2), O(1), C(1), C(2), C(4) group and the planar Re(1), N, C(3), S group at 32.5° is not as large as that in **2a**. Compound **3a** was used to test for the reversibility of the decarbonylation. Compound **2a** was isolated in 85% yield after stirring a solution of **3a** in methylene chloride under 1 atm of carbon monoxide at 25 °C for 12 h.

Treatment of each of compounds **2a–c** with $[Re(CO)_4(\mu\text{-}I)]_2$ in heptane solvent at 80 °C for 5 h resulted in the formation of the new trirhenium complexes $Re_3(CO)_{11}[\mu\text{-}I)[(E)\text{-}HC{=}C(CO_2Me)C(NC_6H_4R){=}S]$ (**4a–c**; R = *p*-Me, H, and *p*-Cl) in the yields 67%, 67%, and 69%, respectively. Compound **4c** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 4. Final fractional atomic coordinates are listed in Table V. Selected interatomic distances and angles are given in Tables VI and VII, respectively. This compound contains a grouping similar to that of **2a–c** less a CO group but has in addition a $Re(CO)_4I$ group that has been added across the Re–S bond. The iodo ligand and the sulfur atom are bridges between the two metal atoms Re(1) and Re(2): Re(1)–I = 2.863(1) Å, Re(2)–I = 2.822(1) Å, Re(1)–S = 2.550(3) Å, Re(2)–S = 2.519(3) Å. The remainder of the molecule is very similar to the corresponding portions found in **2a** and **3a**, but the S–C(1) distance is long as found in **3a** (1.79(1) Å), where the sulfur atom is a bridge. The dihedral angle between the Re(3), O(1), C(4), C(2), C(3) group and the Re(1), N, C(1), S group is closer to that found in **2a**, 42.7°.

A summary of the results of this study is shown in Scheme I. The addition of the aryl isothiocyanates to compound 1 results in the displacement of the acetonitrile ligand and the addition and insertion of the isothiocyanate molecule into the metal–carbon bond of the carboxylate-substituted carbon atom. A thioamido grouping was formed by the formation of a carbon–carbon bond to the isothiocyanate carbon atom. This group chelates to one of the metal atoms and serves as a three-electron donor. There are a number of reports of the insertion of isocyanates into metal–carbon bonds,[1] but the insertion of isothiocyanates into transition-metal–carbon bonds is

Table V. Positional Parameters and *B*(eq) Values for 4c

atom	*x*	*y*	*z*	*B*(eq), Å²
Re(1)	0.18626(02)	0.04228(02)	0.65414(04)	3.13(2)
Re(2)	0.38222(02)	0.07339(02)	0.63978(04)	3.19(2)
Re(3)	0.42385(03)	−0.16898(03)	0.80040(04)	4.28(3)
I	0.27976(04)	0.06265(04)	0.48997(06)	4.06(5)
Cl	0.1069(02)	−0.24964(19)	0.5011(04)	8.2(3)
S	0.29586(14)	0.02669(14)	0.7521(02)	3.1(1)
O(1)	0.3870(04)	−0.1620(04)	0.6408(07)	4.5(5)
O(2)	0.3260(04)	−0.1090(03)	0.5336(07)	3.9(5)
O(11)	0.0668(04)	0.0298(05)	0.5061(08)	6.2(6)
O(12)	0.0920(05)	0.0232(05)	0.8369(07)	6.3(6)
O(13)	0.1583(05)	0.1670(05)	0.6772(09)	6.8(7)
O(21)	0.4535(04)	−0.0348(04)	0.5675(07)	5.3(6)
O(22)	0.3156(05)	0.1821(04)	0.7199(08)	6.3(6)
O(23)	0.4746(05)	0.1391(04)	0.4962(09)	7.0(7)
O(24)	0.4854(05)	0.0809(05)	0.8116(08)	8.4(8)
O(31)	0.5037(07)	−0.2746(06)	0.7574(10)	9.8(9)
O(32)	0.4638(06)	−0.1673(05)	1.0279(08)	7.8(7)
O(33)	0.5467(06)	−0.0936(06)	0.7558(12)	11(1)
O(34)	0.2934(06)	−0.2315(06)	0.8636(13)	11(1)
N	0.2248(05)	−0.0413(05)	0.6523(07)	3.7(5)
C(1)	0.2836(06)	−0.0406(05)	0.6993(09)	3.1(6)
C(2)	0.3323(05)	−0.0846(05)	0.7100(09)	2.8(6)
C(3)	0.3645(06)	−0.0966(05)	0.7993(09)	3.7(7)
C(4)	0.3497(06)	−0.1213(06)	0.6250(10)	3.5(7)
C(5)	0.3413(08)	−0.1463(08)	0.4497(12)	7(1)
C(11)	0.1114(06)	0.0358(06)	0.5621(10)	3.8(7)
C(12)	0.1280(07)	0.0292(06)	0.7676(10)	4.4(8)
C(13)	0.1687(06)	0.1217(07)	0.6670(11)	4.9(8)
C(21)	0.4256(06)	0.0033(06)	0.5925(09)	3.4(7)
C(22)	0.3397(06)	0.1418(06)	0.6896(10)	3.9(7)
C(23)	0.4397(07)	0.1140(06)	0.5496(12)	4.8(8)
C(24)	0.4463(07)	0.0780(06)	0.7497(11)	4.4(7)
C(31)	0.4716(08)	−0.2367(08)	0.7732(14)	7(1)
C(32)	0.4511(07)	−0.1690(07)	0.9426(12)	5.6(9)
C(33)	0.5020(08)	−0.1210(07)	0.7684(13)	6(1)
C(34)	0.3400(09)	−0.2110(07)	0.8391(15)	7(1)
C(41)	0.1946(06)	−0.0919(05)	0.6162(09)	3.2(6)
C(42)	0.1663(06)	−0.0943(06)	0.5201(10)	4.1(7)
C(43)	0.1400(07)	−0.1435(07)	0.4839(12)	6(1)
C(44)	0.1410(07)	−0.1890(06)	0.5460(13)	5.3(9)
C(45)	0.1648(07)	−0.1855(06)	0.6453(12)	5.7(9)
C(46)	0.1927(06)	−0.1377(06)	0.6816(10)	4.3(7)

Table VI. Intramolecular Distances for 4c[a]

Re(1)–I	2.863(1)	N–C(41)	1.45(2)
Re(1)–S	2.550(3)	C(1)–C(2)	1.45(2)
Re(1)–N	2.17(1)	C(2)–C(3)	1.35(2)
Re(2)–I	2.822(1)	C(2)–C(4)	1.46(2)
Re(2)–S	2.519(3)	C(41)–C(42)	1.36(2)
Re(3)–O(1)	2.192(9)	C(41)–C(46)	1.40(2)
Re(3)–C(3)	2.12(1)	C(42)–C(43)	1.39(2)
Cl–C(44)	1.72(1)	C(43)–C(44)	1.36(2)
S–C(1)	1.79(1)	C(44)–C(45)	1.37(2)
O(1)–C(4)	1.25(1)	C(45)–C(46)	1.37(2)
O(2)–C(4)	1.30(1)	Re–C(av)	1.95(2)
O(2)–C(5)	1.44(2)	O–C(av)	1.14(2)
N–C(1)	1.32(1)		

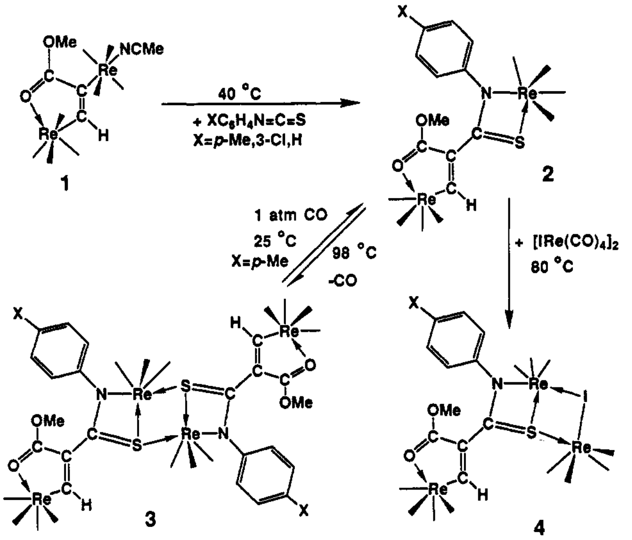
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

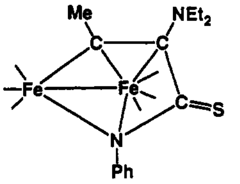
Table VII. Intramolecular Bond Angles for 4c[a]

I–Re(1)–S	80.56(7)	C(1)–C(2)–C(4)	123(1)
I–Re(1)–N	85.6(2)	C(3)–C(2)–C(4)	113(1)
S–Re(1)–N	64.1(3)	Re(3)–C(3)–C(2)	117(1)
I–Re(2)–S	81.89(7)	O(1)–C(4)–O(2)	123(1)
O(1)–Re(3)–C(3)	75.1(4)	O(1)–C(4)–C(2)	120(1)
Re(1)–I–Re(2)	88.82(3)	O(2)–C(4)–C(2)	117(1)
Re(1)–S–Re(2)	103.4(1)	N–C(41)–C(42)	120(1)
Re(1)–S–C(1)	80.2(4)	N–C(41)–C(46)	120(1)
Re(2)–S–C(1)	106.6(4)	C(42)–C(41)–C(46)	120(1)
Re(3)–O(1)–C(4)	114.4(8)	C(41)–C(42)–C(43)	120(1)
C(4)–O(2)–C(5)	117(1)	C(42)–C(43)–C(44)	120(1)
Re(1)–N–C(1)	107.3(9)	Cl–C(44)–C(43)	119(1)
Re(1)–N–C(41)	130.7(8)	Cl–C(44)–C(45)	120(1)
C(1)–N–C(41)	122(1)	C(43)–C(44)–C(45)	120(1)
S–C(1)–N	108(1)	C(44)–C(45)–C(46)	121(1)
S–C(1)–C(2)	123.1(8)	C(41)–C(46)–C(45)	119(1)
N–C(1)–C(2)	129(1)	Re–C–O (av)	177(2)
C(1)–C(2)–C(3)	124(1)		

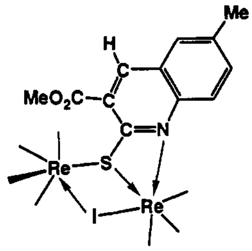
[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Scheme I





5



6

extremely rare.[9] Insertion of organic isothiocyanates into metal–hydrogen bonds has been reported to yield thioformamido ligands.[10] The only previous report of coupling of an organic isothiocyanate to an alkyne ligand was for the reaction of the ynamine complex $Fe_2(CO)_7(\mu\text{-}MeC_2NEt_2)$ with PhNCS to yield the complex $Fe_2(CO)_6[\mu\text{-}MeCC(NEt_2)C(S)NPh]$ (**5**), in which the carbon atom was joined to the amine-substituted carbon.[11] There was no significant formation of the compounds **2a–c** in attempted reactions between **A** and the appropriate isothiocyanate. Thus, we believe that the formation of the compounds **2a–c** from **1** is aided by a facile loss of the acetonitrile ligand. We have shown previously that carboxylate-

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(9) (a) Wilkins, J. D. *J. Organomet. Chem.* **1974**, *65*, 383. (b) Sato, F.; Noguchi, J.; Sato, M. *J. Organomet. Chem.* **1976**, *118*, 117.

(10) Adams, R. D.; Dawoodi, Z.; Foust, D. F.; Segmüller, B. E. *Organometallics* **1983**, *2*, 315.

(11) (a) Crocq, V.; Daran, J.-C.; Jeannin, Y. *J. Organomet. Chem.* **1989**, *373*, 85. (b) Adams, R. D.; Daran, J.-C.; Jeannin, Y. *J. Cluster Sci.* **1992**, *3*, 1.

substituted alkynes react with 1 by displacement of acetonitrile ligand followed by insertion into the metal–carbon bond.

When heated to 98 °C, the compounds **2a–c** lose CO and condense to form the dimeric species, in which the halves of the molecule are joined by bridging sulfur atoms of the thioamido groupings, which then serve as four-electron donors. The dimers can be split by CO to regenerate the original complexes. When **2a–c** are heated in the presence of $[Re(CO)_4(\mu\text{-}I)]_2$, the decarbonylation is accompanied by the addition of a $Re(CO)_4I$ fragment. The sulfur atom and the iodo ligand become bridges and hold the two metal groupings together.

We have recently shown that compound **2a** is converted into the complex $Re_2(CO)_7[\mu\text{-}2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}Me\text{-}NC_9H_4]$-$(\mu\text{-}I)$ (6), containing a quinoline-2-thiolate ligand, when treated with I_2 in the presence of UV radiation.[6] The compounds 4 also undergo this transformation when irradiated (UV), and the iodine is not required. These results will be reported shortly.[12]

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Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for all four structural analyses and tables of bond distances and angles for 1, **2a**, and **3a** (20 pages). Ordering information is given on any current masthead page.

OM9303313

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[12] Adams, R. D.; Chen, L.; Wu, W. *Organometallics*, submitted for publication.